

shown to greatly suppress the formation of silica precipitates and copper stains. Use of the organic chemical substances in a polishing additive solution used during the end portion of the polish cycle has shown similar effects. The elimination or substantial reduction of these defects in the  
5 copper metallization lines will result in improved reliability.

It is not intended that our invention be restricted to the exact embodiments described herein. Use of other chemical substances than those listed, but which share the properties of multiple hydrogen bonds with the surfaces of polymeric silica molecules and/or of copper(hydroxo) species  
10 may be used without altering the inventive concept. These additives may also be used in Ta barrier slurries for copper CMP which use other abrasives such as alumina in place of silica, since the presence of dissolved  $\text{SiO}_2$  CMP byproducts in the slurry medium can also result in precipitates and copper staining. The scope of the invention should be construed in view of the  
15 claims.

WITH THIS IN MIND, WE CLAIM:

1. In a Chemical-Mechanical Polishing (CMP) slurry for polishing Ta barrier layers in integrated circuit metallization structures including copper and silica, said CMP slurry including;

abrasive particles suspended in an aqueous medium; and

5 a copper passivation agent;

the improvement comprising:

said CMP slurry additionally including an organic additive comprising molecules, said additive molecules adsorbing onto and forming a plurality of adsorbant chemical bonds with at least one of the group

10 consisting of said silica and said copper;

said organic additive suppressing chemical reactions between said copper, said silica, and said copper passivation agent.

2. A CMP slurry for polishing Ta barrier layers in integrated circuit metallization structures including copper and silica, said CMP slurry including:

abrasive particles suspended in an aqueous medium;

a copper passivation agent;

an organic additive comprising molecules, said additive molecules

20 adsorbing onto and forming a plurality of adsorbant chemical bonds with at least one of the group consisting of said silica and said copper;

said organic additive suppressing chemical reactions between said silica, said copper, and said copper passivation agent.

25 3. The CMP slurry of claim 2, wherein said abrasive particles are silica.

4. The CMP slurry of claim 3, wherein said copper passivation agent is selected from the group consisting of:

1,2,4-triazole, benzotriazole (BTA), imidazole, 5-methyl benzimidazole, polyaniline, indazole, and purine.

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5. The CMP slurry of claim 4, wherein said adsorbant chemical bonds comprise hydrogen bonds.

6. The CMP slurry of claim 5, wherein said organic additive is selected from the group consisting of:

polyvinyl alcohol (PVA), PVA-poly(vinyl acetate) co-polymer, PVA-polyethylene co-polymer, sorbitol, glycerol, polyacrylamide (PAA), ethylene glycol, di(ethylene glycol), poly(ethylene glycol) (PEG), glycerol ethoxylate (GEO), dimethylsiloxane-ethylene oxide co-polymer (DMSiO-EO), polyethylene oxide surfactants, perfluorinated analogs of polyethylene oxide surfactants, and glycerol propoxylate (GPO).

7. The CMP slurry of claim 6, wherein said organic additive comprises polyvinyl alcohol (PVA).

8. The CMP slurry of claim 7, wherein said PVA is 98% hydrolyzed, and has an average molecular weight in the range between 10,000 and 186,000.

9. The CMP slurry of claim 8, wherein said PVA comprises at least 0.1 weight % of said slurry.

10. The CMP slurry of claim 9, wherein said PVA has an average molecular weight between 13,000 and 23,000, and said PVA comprises between 0.11 and 0.55 weight percent of said slurry.

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11. The CMP slurry of claim 10, comprising:

Cabot SC113;

1.54 wt% 1,2,4-triazole;

0.11 wt% PVA-18000;

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4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

12. The CMP slurry of claim 10, comprising:

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1.54 wt% 1,2,4-triazole;

0.55 wt% PVA-18000;

4.33 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

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13. The CMP slurry of claim 10, comprising:

1.54 wt% 1,2,4-triazole;

0.22 wt% PVA-18000;

4.34 wt% H<sub>2</sub>O;

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0.05 wt% sodium dodecylbenzenesulfonate

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

5 14. The CMP slurry of claim 10, comprising:

1.54 wt% 1,2,4-triazole;

0.55 wt% PVA-18000;

4.33 wt% H<sub>2</sub>O;

0.13 wt% sodium dodecylbenzenesulfonate

10 the remainder of said slurry being Cabot SC113 aqueous silica suspension.

15 15. The CMP slurry of claim 6, wherein said organic additive comprises sorbitol.

16. The CMP slurry of claim 15, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% sorbitol;

4.31 wt% H<sub>2</sub>O;

20 the remainder of said slurry being Cabot SC113 aqueous silica suspension.

17. The CMP slurry of claim 6, wherein said organic additive comprises polyacrylamide (PAA).

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18. The CMP slurry of claim 17, wherein said PAA has an average molecular weight greater than or equal to 1500 and a concentration of at least 0.1 wt%.

5 19. The CMP slurry of claim 18, comprising:

1.54 wt% 1,2,4-triazole;

0.10 wt% PAA-10000;

4.45 wt% H<sub>2</sub>O;

10 the remainder of said slurry being Cabot SC113 aqueous silica suspension.

20. The CMP slurry of claim 18, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% PAA-10000;

15 5.25 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

21. The CMP slurry of claim 18, comprising:

20 1.54 wt% 1,2,4-triazole;

0.10 wt% PAA-1500;

4.45 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

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22. The CMP slurry of claim 18, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% PAA-1500;

5.25 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica  
suspension.

23. The CMP slurry of claim 6, wherein said organic additive comprises  
poly(ethylene glycol) (PEG).

24. The CMP slurry of claim 23, wherein said PEG has an average  
molecular weight greater than or equal to 200 and a concentration of at least  
0.1 wt%.

25. The CMP slurry of claim 24, comprising:

1.54 wt% 1,2,4-triazole;

0.10 wt% PEG-10000;

4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica  
suspension.

26. The CMP slurry of claim 24, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% PEG-10000;

4.31 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica  
suspension.

27. The CMP slurry of claim 24, comprising:

1.54 wt% 1,2,4-triazole;

0.10 wt% PEG-1000;

4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

28. The CMP slurry of claim 24, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% PEG-1000;

4.31 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

29. The CMP slurry of claim 24, comprising:

1.54 wt% 1,2,4-triazole;

0.10 wt% PEG-200;

4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

30. The CMP slurry of claim 24, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% PEG-200;

4.31 wt% H<sub>2</sub>O;



the remainder of said slurry being Cabot SC113 aqueous silica suspension.

31. The CMP slurry of claim 6, wherein said organic additive comprises glycerol ethoxylate (GEO).

32. The CMP slurry of claim 31, comprising:

1.54 wt% 1,2,4-triazole;

0.10 wt% GEO-1000;

4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

33. The CMP slurry of claim 31, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% GEO-1000;

4.31 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

34. The CMP slurry of claim 6, wherein said organic additive comprises di(ethylene glycol) (DEG).

35. The CMP slurry of claim 34, comprising:

1.54 wt% 1,2,4-triazole;

0.10 wt% DEG;

4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

5 36. The CMP slurry of claim 34, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% DEG;

4.31 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica  
10 suspension.

37. The CMP slurry of claim 6, wherein said organic additive comprises a non-ionic surfactant selected from the group consisting of:

dimethylsiloxane-ethylene oxide co-polymer (DMSiO-EO), octylphenol

15 polyethylene oxide, nonylphenol polyethylene oxide, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, and perfluorinated analogs of any of these.

38. The CMP slurry of claim 37, wherein said organic additive comprises

20 dimethylsiloxane-ethylene oxide co-polymer (DMSiO-EO).

39. The CMP slurry of claim 38, wherein said DMSiO-EO has a concentration of at least 0.01 wt%.

25 40. The CMP slurry of claim 39, comprising:

1.54 wt% 1,2,4-triazole;

0.01 wt% DMSiO-EO;

4.36 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

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41. The CMP slurry of claim 39, comprising:

1.54 wt% 1,2,4-triazole;

0.10 wt% DMSiO-EO;

4.35 wt% H<sub>2</sub>O;

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the remainder of said slurry being Cabot SC113 aqueous silica suspension.

42. The CMP slurry of claim 6, wherein said organic additive comprises Glycerol Propoxylate (GPO).

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43. The CMP slurry of claim 42, wherein said GPO has an average molecular weight of at least 260 and a concentration of at least 0.01 wt%.

44. The CMP slurry of claim 43 comprising:

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1.54 wt% 1,2,4-triazole;

0.10 wt% GPO-1500;

4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

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45. The CMP slurry of claim 43 comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% GPO-1500;

4.31 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica  
suspension.

46. The CMP slurry of claim 43 comprising:

1.54 wt% 1,2,4-triazole;

0.10 wt% GPO-260;

4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica  
suspension.

47. The CMP slurry of claim 43 comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% GPO-260;

4.31 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica  
suspension.

48. The CMP slurry of claim 4, wherein said adsorbant chemical bonds are  
selected from the group consisting of hydrogen bonds and electrostatic  
bonds.

49. The CMP slurry of claim 48, wherein said adsorbant chemical bonds  
are electrostatic bonds.

50. The CMP slurry of claim 49, wherein said organic additive is an organic amine.

5 51. The CMP slurry of claim 50, wherein said organic additive is N,N-diethylcyclohexylamine (DCA).

52. The CMP slurry of claim 51, comprising:

1.54 wt% 1,2,4-triazole;

10 0.10 wt% DCA;

4.35 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

15 53. The CMP slurry of claim 51, comprising:

1.54 wt% 1,2,4-triazole;

1.00 wt% DCA;

4.30 wt% H<sub>2</sub>O;

20 the remainder of said slurry being Cabot SC113 aqueous silica suspension.

54. The CMP slurry of claim 50, wherein said organic additive is polyethyleneimine (PEI) having an average molecular weight of 1800.

25 55. The CMP slurry of claim 54, comprising:

1.54 wt% 1,2,4-triazole;

0.013 wt% PEI-1800;

4.37 wt% H<sub>2</sub>O;

the remainder of said slurry being Cabot SC113 aqueous silica suspension.

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56. A Chemical-Mechanical Polishing (CMP) method for polishing Ta barrier layers in integrated circuit metallization structures including copper and silica, said method including flowing polishing slurry containing silica abrasive, DI water, and a copper passivation agent, onto a platen, inducing relative motion between said wafer and said platen and maintaining a force between said platen and said wafer, and removing said wafer from against said platen, said polishing occurring for a total polishing period of time, comprising,

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said polishing slurry further containing, for at least a portion of said total polishing period of time, an organic additive selected from the group consisting of:

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polyvinyl alcohol (PVA), PVA-poly(vinyl acetate) co-polymer, PVA-polyethylene co-polymer, sorbitol, glycerol, polyacrylamide (PAA), ethylene glycol, di(ethylene glycol), poly(ethylene glycol) (PEG), glycerol ethoxylate (GEO), dimethylsiloxane-ethylene oxide co-polymer (DMSiO-EO), polyethylene oxide surfactants, octylphenol polyethylene oxide, nonylphenol polyethylene oxide, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, perfluorinated analogs of polyethylene oxide surfactants, glycerol propoxylate (GPO),

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organic amines, N,N-diethylcyclohexylamine (DCA), and polyethyleneimine (PEI).

57. The method of claim 56, wherein said at least a portion of said total  
5 polishing period of time is the entire said total polishing period of time.

58. The method of claim 56, wherein said at least a portion of said total  
polishing period of time is substantially equal to or less than the last 10% of  
said total polishing period of time.

10 59. The method of claim 58, wherein said polishing slurry containing said  
organic additive is formed by Point-of-Use (POU) mixing of said organic  
additive with said polishing slurry containing said DI water, said silica  
abrasive, and said Cu passivation agent.

15 60. The CMP method of claim 59, wherein said organic additive comprises  
PEG-10000 and said Cu passivation agent comprises 1,2,4-triazole.

20 61. The CMP method of claim 60, wherein said polishing slurry containing  
said organic additive comprises:

1.54 wt % 1,2,4-triazole;

0.5 wt% PEG-10,000;

93.6 wt % silica suspension containing 13.6 wt% SiO<sub>2</sub>;

4.33 wt% DI water.

25 62. A polishing additive solution comprising,

DI water;

a copper passivation agent selected from the group consisting of,

1,2,4-triazole, benzotriazole (BTA), imidazole, 5-methyl  
benzimidazole, polyaniline, indazole, and purine;

an organic additive selected from the group consisting of:

polyvinyl alcohol (PVA), PVA-poly(vinyl acetate) co-polymer,  
PVA-polyethylene co-polymer, sorbitol, glycerol,  
polyacrylamide (PAA), ethylene glycol, di(ethylene glycol),  
poly(ethylene glycol) (PEG), glycerol ethoxylate (GEO),  
dimethylsiloxane-ethylene oxide co-polymer (DMSiO-EO),  
polyethylene oxide surfactants, octylphenol polyethylene  
oxide, nonylphenol polyethylene oxide, polyoxyethylene lauryl  
ether, polyoxyethylene cetyl ether, perfluorinated analogs of  
polyethylene oxide surfactants, glycerol propoxylate (GPO),  
organic amines, N,N-diethylcyclohexylamine (DCA), and  
polyethyleneimine (PEI).

63. In a Chemical-Mechanical Polishing (CMP) method for polishing Ta  
barrier layers in integrated circuit metallization structures including copper  
and silica, said method including flowing polishing slurry containing silica  
abrasive, DI water, and a copper passivation agent onto a platen, inducing  
relative motion between said wafer and said platen while maintaining a  
force between said platen and said wafer, and removing said wafer from  
against said platen, said polishing occurring for a first polishing period of  
time, the improvement comprising:



decreasing said flow of said polishing slurry prior to said step of removing said wafer from against said platen; and

flowing the polishing additive solution of claim 62 onto said platen for a second period of time while inducing relative motion between said  
5 wafer and said platen and maintaining a force between said platen and said wafer..

64. The method of claim 63 wherein the step of decreasing said flow of said slurry decreases said flow to zero.

10 65. The CMP method of claim 63, wherein said organic additive comprises PEG-10,000 and said copper passivation agent comprises 1,2,4-triazole.

66. The CMP method of claim 63, wherein said steps of decreasing said  
15 flow of said polishing slurry and flowing of said polishing additive solution are performed just prior to wafer de-chuck operation.

67. The CMP method of claim 66, wherein the step of decreasing said flow of said slurry decreases said flow to zero.

20 68. The CMP method of claim 67, wherein said organic additive comprises PEG-10,000 and said copper passivation agent comprises 1,2,4-triazole.

69. The CMP method of claim 68, wherein said polishing additive solution  
25 comprises:

3.0 wt % 1,2,4-triazole;

0.5 wt % PEG- 10,000, and  
DI water.

70. The CMP method of claim 63, wherein said steps of decreasing said  
5 flow of said polishing slurry and flowing of said polishing additive solution  
are performed just prior to post-Ta CMP buff operation.

71. The CMP method of claim 70, wherein the step of decreasing said flow  
of said slurry decreases said flow to zero.

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72. The CMP method of claim 71, wherein said organic additive comprises  
PEG-10,000 and said copper passivation agent comprises 1,2,4-triazole.

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73. The CMP method of claim 72, wherein said polishing additive solution  
comprises:

2.0 - 3.0 wt % 1,2,4-triazole;  
0.1 – 2.0 wt % PEG-10,000, and  
DI water;

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and wherein said post-CMP buff step utilizes 0.5 – 2.0 psi down force for 5  
– 30 seconds.